

Kinetics of Phase ordering in Microemulsions and Micellar Solutions

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We review the models developed and techniques used in recent years to study the kinetics of phase ordering in a class of complex fluids, namely, ternary microemulsions and micellar solutions.

I. INTRODUCTION

The “head” part of surfactant molecules consist of a polar or ionic group. The “tail” of many surfactants consist of a single hydrocarbon chain whereas that of some other surfactants, e.g., phospholipids, are made of two hydrocarbon chains both of which are connected to the same head¹. In contrast, *gemini* surfactants^{2–5}, consist of two single-chain surfactants whose heads are connected by a “spacer” chain and, hence, these “double-headed” surfactants are sometimes also referred to as “dimeric surfactants”^{6,7} (see fig.1).

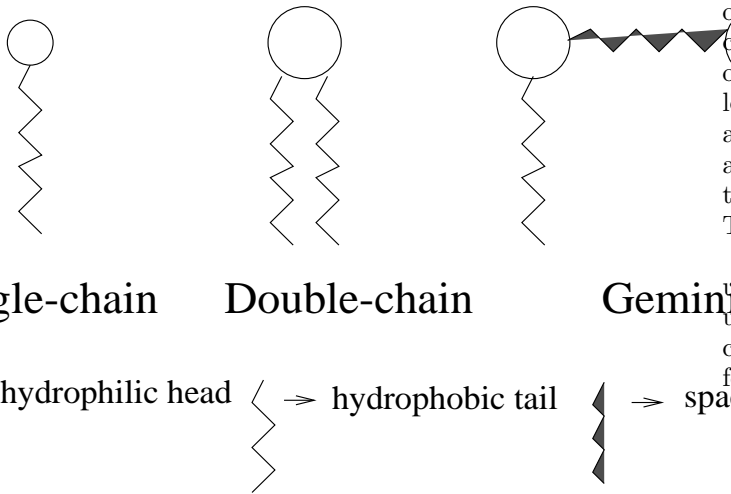


FIG. 1. Different types of amphiphiles.

When put into an aqueous medium, the “heads” of the surfactants like to get immersed in water and, hence, are called “hydrophilic” while the tails tend to minimize contact with water and, hence, are called “hydrophobic”¹. The spacer in gemini surfactants is usually hydrophobic but gemini surfactants with hydrophilic spacers have also been synthesized⁸. Surfactant molecules are called “amphiphilic” because their heads are “water-loving” and hydrocarbon chains are “water-hating”. Because of their amphiphilicity the surfactant molecules form “*self-assemblies*” (i.e., supra-molecular aggregates), such as monolayer and bilayer membranes, micelles, inverted-micelles, etc.⁹, in a multi-component fluid mixture con-

taining water. These not only find wide ranging applications in detergent and pharmaceutical industries, food technology, petroleum recovery, etc. but are also one of the most important constituents of cells in living systems. Therefore, physics, chemistry, biology and technology meet at the frontier area of interdisciplinary research on association colloids formed by surfactants¹¹.

A ternary microemulsion is a “colloidal” complex fluid consisting of three components, namely, oil, water and surfactants; the phase diagrams of such ternary systems have been studied extensively^{10,9}. When the concentration of the amphiphilic molecules is sufficiently high, the low-temperature equilibrium phase of the system is lamellar where the amphiphiles arrange themselves in (approximately) parallel stacks. On the other hand, when the concentration of the amphiphiles is not high, the system exhibits either a droplet phase or a bicontinuous microemulsion phase in equilibrium at sufficiently low temperatures depending on the relative concentrations of oil and water. If the concentrations of oil and water are comparable then the bicontinuous microemulsion phase is observed. But, if the concentration of oil (water) is much less than that of water (oil) then droplets of oil (water) are found to be dispersed in water (oil); these droplets are often referred to as micelles and, therefore, the system under such conditions are called micellar solution. These systems find wide ranging industrial applications.

The aim of this chapter is to present a systematic and upto date review of the models developed and techniques used so far to study the kinetics of phase ordering in microemulsions and micellar solutions (see references^{12–15} for earlier reviews).

II. KINETICS OF ORDERING IN BINARY MIXTURES IN THE ABSENCE OF SURFACTANT IMPURITIES

We introduce the key concepts involved in the studies of phase ordering by illustrating them with the help of binary mixtures. The techniques used so far for the studies of phase ordering in ternary microemulsions and micellar solutions are extensions of those used widely for the corresponding studies in the simpler case of binary mixture of immiscible components, e.g., binary alloys, binary fluids, etc. Therefore in this section we classify and summarize the main techniques used for such studies^{16–21}.

Suppose a binary alloy has been quenched from a high temperature T_h to a temperature T_ℓ well below the coexistence curve. The morphology of the coarsening domain

“pattern” depends on the relative concentrations of the two components. If the concentrations of the two components are comparable then the pattern has a random “interconnected” structure. On the other hand, if the concentration of one of the components is much smaller than that of the other the pattern consists of “droplets” of various sizes.

There are essentially two different (albeit complementary) theoretical approaches to the study of the kinetics of the phase ordering processes, viz., microscopic models and phenomenological models.

A. Microscopic Models

Two types of microscopic models have been used; the molecular models defined on a continuum and lattice models.

1. Molecular Models on a Continuum:

For the Molecular Dynamics simulation of an immiscible binary mixture of two species, labelled A and B , one first postulates an approximate form of inter-molecular interactions, e.g., truncated Lennard-Jones potentials. The potentials are chosen in such a manner that the interactions $A-A$ and $B-B$ are attractive while the interaction $A-B$ is repulsive²². Normally one uses the Verlet algorithm for integrating Newton’s equation of motion²³. In principle, one can use either a constant-energy ensemble or a constant temperature ensemble.

2. Microscopic Lattice Models

The binary alloys can be modelled as an Ising spin system where $S_i = 1$ correspond to an A atom and $S_i = -1$ correspond to an B atom. In the symmetric case, i.e., when $E_{AA} = E_{BB}$, the Hamiltonian for the system is given by

$$H = -J \sum S_i S_j \quad (1)$$

where $J > 0$ and the summation is to be carried out over all the distinct nearest-neighbour spin pairs. However, no such model is complete without specification of the prescription for the dynamical evolution of the system²⁴. In the case of binary alloys, unlike the magnetic counterpart, the order parameter is conserved, i.e., the concentrations of A atoms and B atoms remains unaltered during the time evolution in a closed system. The kinetics of ordering in such a system can be studied at a microscopic level by using the so-called Kawasaki spin-exchange dynamics: two anti-parallel nearest-neighbour spins can exchange their position with a probability $1/[1 + \exp(\beta\Delta E)]$, with $\beta = 1/(k_B T)$ where k_B is the

Boltzmann constant and ΔE is the energy change that would be caused by the interchange of the two spins.

B. Phenomenological Models with Langevin Dynamics

In the phenomenological approach the system is described by an order parameter field $\psi(\vec{r})$, which is the local difference in the concentrations of the A and B atoms. In contrast to the discrete allowed values of the spins in the lattice model, the order parameter can take all real values in the interval $-1 \leq \psi \leq 1$. The coarse-grained free-energy functional for the d -dimensional system is given by

$$F[\psi(\vec{r})] = \int d^d r [r_0 \psi^2(\vec{r}) + u \psi^4(\vec{r}) + c |\nabla \psi(\vec{r})|^2] \quad (2)$$

where r_0, u and c are phenomenological coefficients. The symmetry requirements rule out the possibility of ψ and ψ^3 terms in this functional. The dynamics of the system is assumed to be governed by the so-called Langevin equation

$$\partial \psi(\vec{r}, t) / \partial t = \Gamma \nabla^2 [\delta F / \delta \psi(\vec{r}, t)] + \eta(\vec{r}, t) \quad (3)$$

where Γ is the phenomenological kinetic coefficient, $\delta / \delta \psi$ denotes the functional derivative with respect to ψ and the Laplacian takes care of the fact that the order parameter is conserved. $\eta(\vec{r}, t)$ is the noise, which is usually assumed to be of ‘Gaussian white’ nature, i.e.,

$$\langle \eta(\vec{r}, t) \eta(\vec{r}', t') \rangle = 2k_B T \nabla^2 \delta(\vec{r} - \vec{r}') \delta(t - t') \quad (4)$$

where $k_B T$ guarantees the approach to the true Gibbsian equilibrium. In the context of the binary alloys the equation (3) is called the Cahn-Hilliard-Cook equation for historical reasons. The model described by the equations (2) - (4) is usually referred to as the model B ²⁵. The computation becomes much more efficient (i.e., the morphological characteristic of the asymptotic regime can be obtained with a very short computer time) by solving equation (3) above by the cell dynamics method²⁶.

C. Characteristic Quantities of Interest

Two quantities are most important in describing the kinetics of this growth process, viz., the time dependence of the typical linear size $R(t)$ of the ordered regions and the dynamic scaling of the structure factor $\mathcal{S}(\vec{q}, t)$ characterizing the statistical self-similarity of the coarsening pattern at different times. The structure factor is the Fourier transform of the two-point correlation function in real space, i.e.,

$$\mathcal{S}(\vec{q}, t) = \sum_{\vec{r}} G(\vec{r}, t) \exp(i\vec{q} \cdot \vec{r}) \quad (5)$$

where $G(\vec{r}, t) = \langle S(\vec{0}, t)S(\vec{r}, t) \rangle - \langle S \rangle^2$ is the correlation function in real space. However, since numerical computations are carried out either on discrete lattices (in the case of microscopic models) or on discrete grids (in the case of phenomenological models) the corresponding structure factor is given by

$$\mathcal{S}(\vec{q}, t) = \langle |(1/N) \sum_{\vec{r}_i} G(\vec{r}_i, t) \exp(i\vec{q} \cdot \vec{r}_i)|^2 \rangle \quad (6)$$

with $\vec{q} = (2\pi/L)(mx + ny + pz)$ and $m, n, p = 1, 2, 3, \dots, L$.

Following a rapid quench from a very high temperature to a temperature below the coexistence curve, coarsening of ordered domains takes place and, consequently, the first zero crossing of $G(R, t)$ (i.e., the smallest R for which $G(R, t) = 0$) occurs at larger and larger values of R at successively longer values of time t , where $G(R, t)$ is the circularly averaged two-point correlation function. As a result, the location of the first zero crossing of $G(R, t)$ may be taken as a measure of $R(t)$.

During the coarsening process the position of the peak in $\mathcal{S}(q, t)$ keeps moving towards smaller values of q where $\mathcal{S}(q, t)$ is circularly averaged. The dynamical scaling form of the structure factor is given by

$$\mathcal{S}(q, t) = R^d F(qR(t)) \quad (7)$$

where $F(x)$ is a function of $x = qR(t)$. The length $R(t)$ can be extracted from $\mathcal{S}(q, t)$ in several different ways:

(i) $R^{-1}(t) = k_m/2\pi$, where k_m is the location of the maximum of the structure factor $\mathcal{S}(q, t)$, (ii) $2\pi/R$ may be identified with the first moment of the structure factor or the square root of the second moment of the structure factor, etc. These measures of $R(t)$ can also be used in the case of ternary microemulsions and micellar solutions. Moreover, one can compute the mean-cluster size of a particular component, say A , using the definition

$$\chi_A = \left[\sum_{s=1}^{s_{max}-1} s^2 n(s) \right] / \left[\sum_{s=1}^{s_{max}} s n(s) \right] \quad (8)$$

where $n(s)$ is the number of clusters of type A with s sites and s_{max} is the corresponding size of the largest cluster.

For binary alloys, for which the order parameter is conserved, i.e., for model B , the length $R(t)$ has been found to follow the growth law

$$R(t) \sim t^n \quad (9)$$

where $n = 1/3$. In contrast, for systems with non-conserved scalar order parameter (model A) $n = 1/2$. Moreover, in case of binary fluids hydrodynamic effects lead to the growth law (9) with $n = 1$. Furthermore,

$$R(t) \sim (\log t)^x, \quad (10)$$

with dimensionality-dependent exponent x , in phase separating binary systems in the presence of quenched disorder (e.g., impurities)²⁷.

III. KINETICS OF ORDERING IN TERNARY MICROEMULSIONS AND MICELLAR SOLUTIONS

In our discussion of the kinetics of phase ordering in ternary microemulsions and micellar solutions we shall begin with the molecular models, which are truly microscopic description of the system, and then consider models at a coarser level and, finally, consider phenomenological models.

A. Molecular Dynamics Simulations of Molecular Models on a Continuum

Laradji et al.²⁸ have carried out a MD simulation of phase separation in a binary mixture in the presence of surfactants. The interaction potential between two molecules i and j (oil-oil, water-water or oil-water) is assumed to be

$$U(\vec{r}_{ij}) = 4\epsilon[(\sigma/r_{ij})^{12} - (2\delta_{\alpha_i\alpha_j} - 1)(\sigma/r_{ij})^6] \quad (11)$$

where $\delta_{\alpha_i\alpha_j}$ is the Kronecker delta function and α_i denotes the type of the molecule i , i.e., $\alpha_i = 1$ for a water molecule and 2 for an oil molecule. Thus, the potential above ensures that molecules of different species always interact repulsively. For example, if $\alpha_i \neq \alpha_j$,

$$U(\vec{r}_{ij}) = 4\epsilon[(\sigma/r_{ij})^{12} + (\sigma/r_{ij})^6] \quad (12)$$

On the other hand, if $\alpha_i = \alpha_j$,

$$U(\vec{r}_{ij}) = 4\epsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6] \quad (13)$$

In this model the “water-loving” head of every surfactant molecule is treated as identical to a water molecule and the “oil-loving” tail is treated as identical to an oil molecule. In other words, every surfactant molecule is assumed to be, effectively, a diatomic molecule one part of which is water-like and the other part is oil-like; the two parts of the molecule are assumed to be connected to each other by a harmonic spring so that the potential is given by

$$U_{ss}(\vec{r}) = (K_s/2)(r_{ij} - \ell_s)^2. \quad (14)$$

To our knowledge, this type of models were first proposed by Smit et al.²⁹. However, Laradji et al.²⁸ was the first to study the kinetics of phase ordering by MD simulation of such a model. A non-zero concentration of amphiphiles was found to slow down the coarsening process leading to a significant deviation from the power-law (9).

B. Microscopic Lattice Models

1. Widom Model: a Spin-1/2 Ising Model on Simple-Cubic Lattice with Farther-Neighbour Interactions

Widom model³⁰ is the simplest lattice model of ternary mixtures of oil, water and surfactants. This is a lattice model in the same spirit as, for example, the lattice model of binary alloys. However, in contrast to the lattice model of binary alloys described in the preceding section, the molecules of oil, water and surfactants in this model are located on the bonds rather than on the lattice sites. In this model the molecules of oil, water and surfactants are represented by the nearest-neighbour bonds of a spin-1/2 Ising model where every spin interacts with the nearest-neighbour as well as a specific subset of farther-neighbour spins. The bonds between the up-up nearest-neighbour spin pairs represent water molecules, those between down-down nearest-neighbour spin pairs represent oil molecules and those between antiparallel nearest-neighbour spin pairs denote the surfactant molecules. The Hamiltonian for this model is given by

$$\mathcal{H} = -J \sum_{\langle ij \rangle} S_i S_j - 2M \sum_{\langle ik \rangle} S_i S_k - M \sum_{\langle il \rangle} S_i S_l \quad (15)$$

where, for three dimensional systems, the summations in the first, second and third terms on the right hand side are to be carried out over the nearest-neighbour, second-neighbour and fourth-neighbour spin pairs, respectively, on a simple cubic lattice. The interaction J is positive (ferromagnetic in the terminology of spin models of magnetic materials) whereas M is negative (antiferromagnetic). The farther-neighbour interactions arise from a prescription, suggested by Widom³⁰, to take into account the bending rigidity of the amphiphilic monolayer membrane at the oil-water interface. This model reduces to the standard spin-1/2 Ising model with only nearest-neighbour ferromagnetic interactions on a simple cubic lattice if $M = 0$.

For studying the dynamics of the Widom model Morawietz et al.³¹ introduced a Kawasaki-type spin exchange dynamics which conserves the molecules of oil, water and surfactants. Note that in this algorithm the spins on the lattice sites, rather than the molecules on bonds, are exchanged; however, the algorithm is such that it leads to simultaneous exchange of three molecules while satisfying the condition that the number of molecules of each species remains conserved. The algorithm is as follows: a up-spin can exchange its position with one of its down-spin neighbours, with probability $1/(1 + \exp(\beta E))$, provided the numbers of up and down spins among the neighbours of the first spin (excluding the second spin, which is also a neighbour of the first) are the same as the neighbours of the second spin (excluding the first spin, which is also a neighbour of the second).

Using this new algorithm, Morawietz et al.³¹ investigated the kinetics of dis-ordering, rather than the traditional study of ordering, by reverse quenching the system

from the ordered phase to the disordered phase. More specifically, an initial configuration was created where a layer of surfactants in the central part of the system is sandwiched between a column of oil above and a column of water below. The parameters $J/(k_B T)$ and $M/(k_B T)$ were so chosen that the corresponding equilibrium phase is known to be a disordered fluid. To our knowledge, the kinetics of ordering in the Widom model has never been studied.

2. Kawakatsu-Kawasaki Model: a Decorated Spin-1/2 Ising Model

The Alexander model³² is a decorated spin-1/2 model, which was extended by Chen et al.³³ for a more realistic description of ternary microemulsions. Kawakatsu and Kawasaki³⁴ have studied the kinetics of phase ordering using a decorated spin-1/2 model which may be regarded as a simplified special case of the model considered by Chen et al.³³. In this model every lattice site is occupied by a Ising spin; $S_i = 1$ corresponds to a water molecule and $S_i = -1$ corresponds to a oil molecule at the i -th site. Just as in the molecular models mentioned in the preceding section, the “water-loving” head part and the “oil-loving” tail part of each surfactant is assumed to be identical to a water molecule and an oil molecule, respectively. A fraction of the nearest-neighbour pairs of dissimilar molecules are connected by a rigid bond; each of the dumb bell-like structures where a rigid bond connects two dissimilar molecules at its two ends is identified as a surfactant. Thus, in this model, the molecules of oil and water occupy the lattice sites whereas the surfactants are located on the bonds. The Hamiltonian for this model is given by

$$\mathcal{H} = (J/2) \sum (1 - S_i S_j) \quad (16)$$

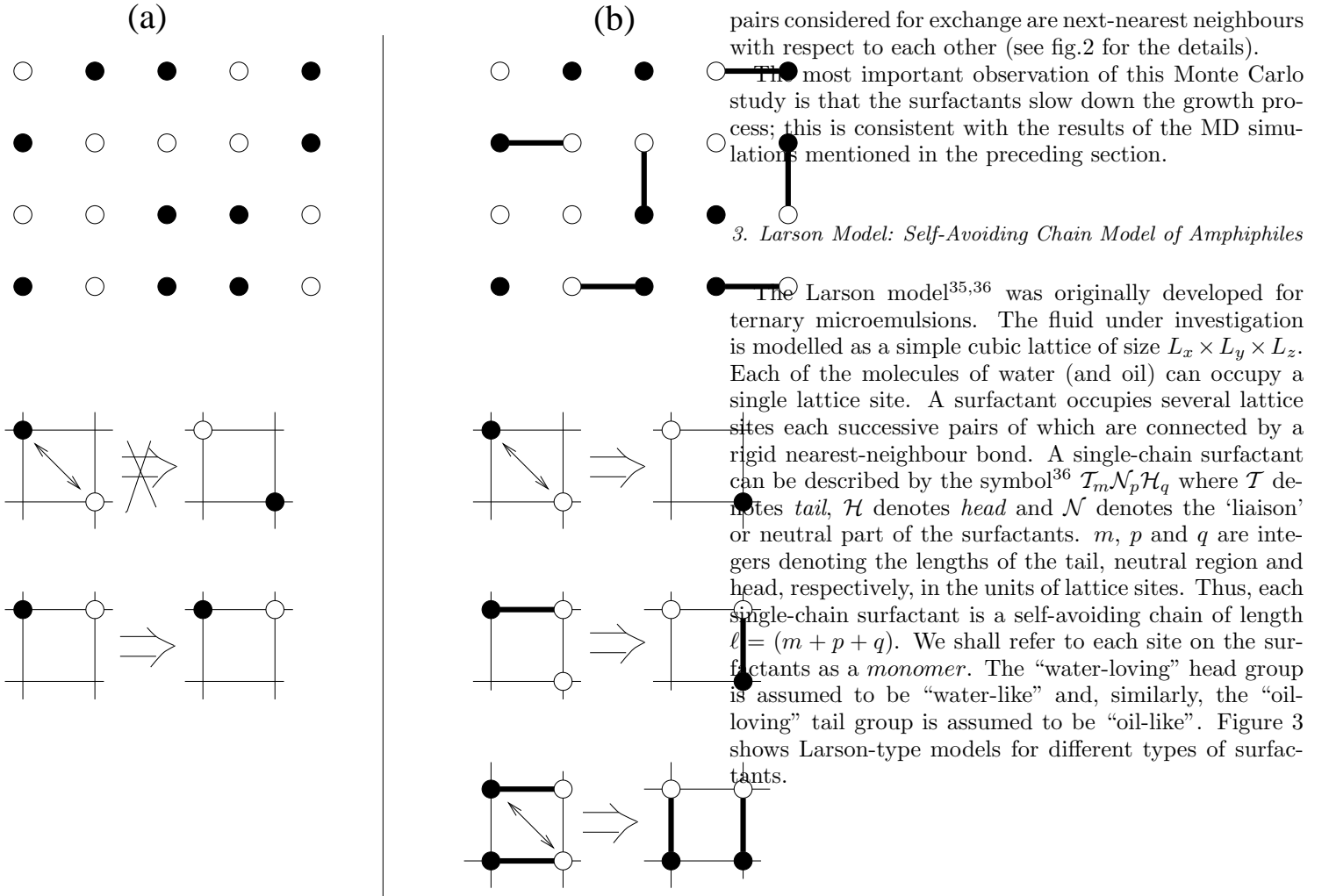
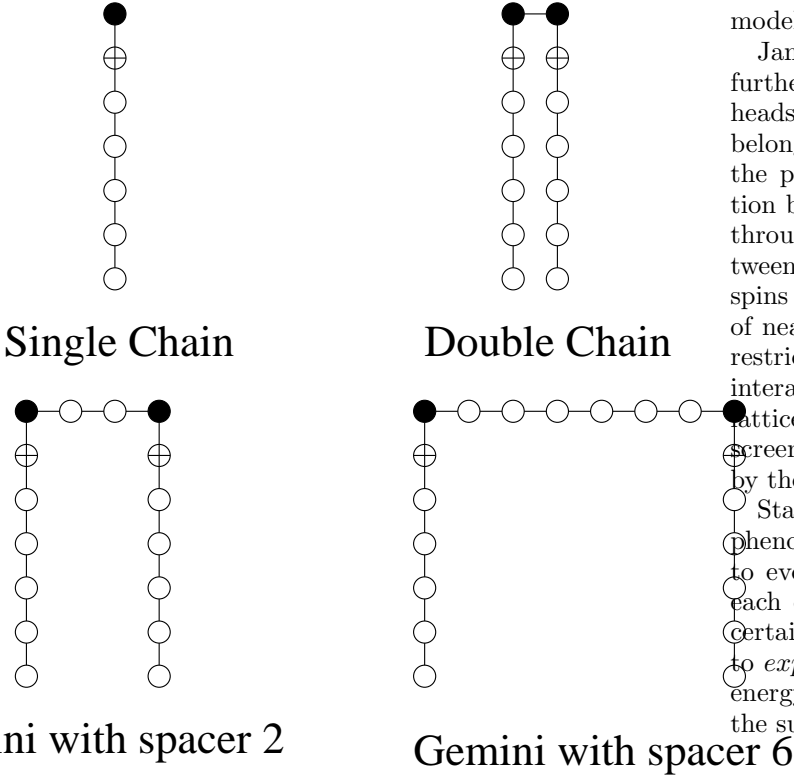


FIG. 2. Schematic representations of (a) the lattice model of a binary alloy and (b) the Kawakatsu-Kawasaki lattice model of a ternary system where one of the components is a surfactant. The elementary ‘exchange’ processes allowed in the dynamics of the two models are also shown. Exchange of anti-parallel nearest neighbours only is allowed in the case of the binary alloy whereas exchange of antiparallel next-nearest neighbours only is allowed in the case of ternary system

Note that the energy of the water-water, oil-oil and water-oil interactions are given by $E_{ww} = 0 = E_{oo}$ and $E_{wo} = J$. Since $J > 0$, water and oil tend to phase separate in the absence of surfactants. Since the two ends of the surfactants are not allowed to split into two separate water and oil molecules during the time evolution of the system the interaction energy between the water-like end and oil-like end of such a surfactant does not affect the dynamics. However, the dynamics must distinguish between individual water (and oil) molecules and the water-like (and oil-like) ends of surfactants so as not to split a surfactant into a water molecule and a oil molecule. The crucial feature of the Kawakatsu-Kawasaki dynamics, which distinguishes it from the Kawasaki spin-exchange dynamics for binary alloys, is that the anti-parallel spin



● Head ○ Tail/Spacer ⊕ Liaison
FIG. 3. Larson-type models of single-chain, double-chain and gemini surfactants.

Jan, Stauffer and collaborators³⁷ simplified the Larson model by formulating it in terms of Ising-like variables in the same spirit in which a large number of simpler lattice models had been formulated earlier³⁸ for the convenience of calculations. In this reformulation, a classical Ising spin variable S is assigned to each lattice site; $S_i = 1$ (-1) if the i -th lattice site is occupied by a water (oil) molecule. If the j -th site is occupied by a monomer belonging to a surfactant then $S_j = 1, -1, 0$ depending on whether the monomer at the j th site belongs to head, tail or neutral part. The monomer-monomer interactions are taken into account through the interaction between the corresponding pair of Ising spins which is assumed to be non-zero provided the spins are located on the nearest-neighbour sites on the lattice. Thus, the Hamiltonian of the system is given by the standard form

$$H = -J \sum_{\langle ij \rangle} S_i S_j. \quad (17)$$

where attractive interaction (analogue of the ferromagnetic interaction in Ising magnets) corresponds to $J > 0$ and repulsive interaction (analogue of antiferromagnetic interaction) corresponds to $J < 0$ ³⁷. The temperature T of the system is measured in the units of J/k_B where k_B is the Boltzmann constant. The Kawakatsu-Kawasaki model may be regarded as a special case of the Larson

model, namely, $m = q = 1$, $p = 0$.

Jan, Stauffer and collaborators³⁷ extended the model further to describe single-chain surfactants with *ionic* heads. According to their formulation, the monomers belonging to the ionic heads have Ising spin $+2$ to mimic the presence of electric charge. The repulsive interaction between a pair of ionic heads is taken into account through an (antiferromagnetic) interaction $J = -1$ between pairs of nearest neighbour sites both of which carry spins $+2$; however, the interaction between all other pairs of nearest-neighbour spins is assumed to be $J = 1$. By restricting the range of the repulsive (antiferromagnetic) interaction between the “charged” heads to only one lattice spacing one is, effectively, assuming very strong screening of the Coulomb repulsion between ionic heads by the counterions.

Starting from an initial state (which depends on the phenomenon under investigation), the system is allowed to evolve following the standard Metropolis algorithm: each of the attempts to move a surfactant takes place certainly if $\Delta E < 0$ and with a probability proportional to $\exp(-\Delta E/T)$ if $\Delta E \geq 0$, where ΔE is the change in energy that would be caused by the proposed move of the surfactant under consideration.

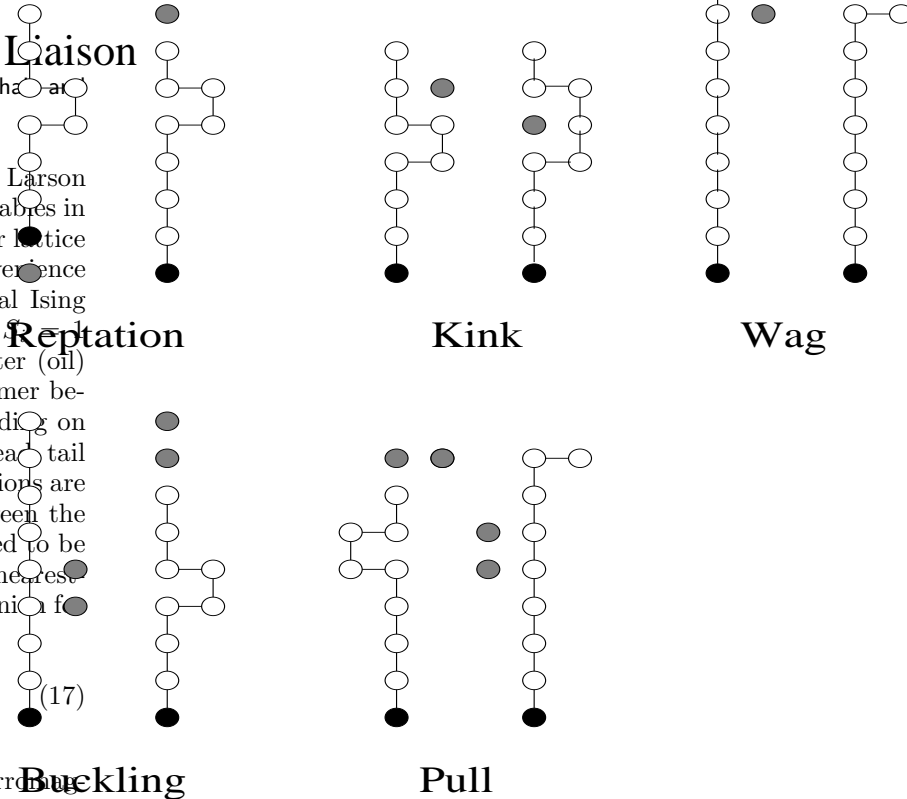


FIG. 4. Different moves of the amphiphiles

Next, we specify the allowed moves of the surfactants

for the appropriate sampling of the states of the system in a MC simulation. So far as the single-chain surfactants are concerned, the moves allowed for the surfactants are as follows: (see fig. 4)

- (i) *reptation*: one of the two ends of each surfactant is picked up randomly, with equal probability, and the surfactant is allowed to move forward along its own contour by one lattice spacing with the probability mentioned above; this move effectively mimics the reptile-like slithering of the surfactants and hence the name;
- (ii) *spontaneous chain buckling*: a portion in the middle of the tail is randomly picked up and allowed to buckle with the probability mentioned above;
- (iii) *kink movement*: a kink formed by the buckling or reptation is allowed to move to a new position with the appropriate probability calculated according to the prescription mentioned above;
- (iv) *pull move*: this is the reverse of spontaneous chain buckling; a buckled part of the tail is pulled so as to make it more extended. Each of these moves is possible only if the new positions of all the monomers are not occupied simultaneously by monomers belonging to other surfactants. Each surfactant is allowed to try each of the above mentioned moves once during each MC step.

Note that the monomers of the same surfactant as well as different surfactants are not allowed to occupy the same lattice site simultaneously; this represents a hard-core intra-chain as well as inter-chain repulsion for monomer separations smaller than one lattice spacing. Moreover, at any non-vanishing temperature, during the out-of-line thermal fluctuations of the chains, the hard-core repulsion leads to steric repulsion between the chains. To our knowledge, no potential energies associated with the torsion of the surfactant chains have been incorporated so far in any work on Larson-type models.

A microscopic lattice model of double-chain surfactants (with a single head) in aqueous solution was developed by Bernardes³⁹ by modifying the Larson model of single-chain surfactants^{35,37,36}. In terms of the symbols used above to denote the primary “structure” of the microscopic lattice model of single-chain surfactants, Bernardes’ lattice model of double-chain surfactants, with a single hydrophilic head, can be described by the symbol $\mathcal{T}_m \mathcal{N}_p \mathcal{H}_q \mathcal{N}_p \mathcal{T}_m$. Very recently, Maiti and Chowdhury⁴⁰ have proposed a microscopic lattice model of gemini surfactants by extending Bernardes’ model so as to incorporate two hydrophilic heads connected by a *spacer*. This model of a gemini surfactant can be represented by the symbol $\mathcal{T}_m \mathcal{N}_p \mathcal{H}_q \mathcal{S}_n \mathcal{H}_q \mathcal{N}_p \mathcal{T}_m$ where n is the number of lattice sites constituting the spacer represented by the symbol \mathcal{S} and the other symbols have the same meaning as in the case of Bernardes’ model of double-chain surfactants (see fig.3). For the convenience of computation, the Bernardes’ model of double-chain surfactants as well as Maiti and Chowdhury’s model of gemini surfactants have also been formulated in terms of classical Ising spin variables, generalizing the corresponding formulation for the single-chain surfactants reported

in ref³⁷.

To our knowledge, the work of Bernardes et al.⁴¹ is the only published report of the investigation on the kinetics of phase ordering in the Larson model of microemulsions. Oil, water and surfactant molecules were distributed randomly in the initial state of the system. The system was allowed to evolve by implementing the moves of the surfactants according to the algorithm mentioned earlier while the molecules of oil and water were allowed to exchange their positions according to the Kawasaki-spin exchange dynamics mentioned earlier in the context of binary mixtures. The time evolution of the mean sizes of the clusters of oil, water and amphiphiles in the system were observed up to 200,000 MC steps.

When the amphiphile concentration $\phi_a = 0.1$ and the concentrations of oil and water $\phi_o = \phi_w = 0.45$, respectively, the average length scale $\langle R \rangle_{ow} = [(1/2)(\chi_o + \chi_w)]^{1/3}$ was found to obey the power law $\langle R \rangle_{ow} \sim t^n$ with $n \simeq 1/3$, i.e., the coarsening was found to be governed by the same Lifshitz-Slyozov law which governs the coarsening in binary mixtures in the absence of amphiphiles. However, comparing these results with the corresponding results obtained by other groups using various different techniques, we believe that the truly asymptotic logarithmically slow growth regime lies beyond the longest time scales of observation in the computer experiments of Bernardes et al.

The kinetics of ordering in microemulsions and micellar solutions containing gemini surfactants have not been reported so far. A microscopic model for single-chain surfactants at the air-water interface has been developed earlier by one of us^{42,43} by appropriately modifying the Larson model^{35,37,36} of ternary microemulsions^{10,9}. Later Maiti and Chowdhury replaced the single-chain surfactants in the model introduced in ref.⁴² by the model gemini surfactants, thereby getting the desired microscopic model of gemini surfactants at the air-water interface. A novel entropy-driven phase segregation has been observed in computer experiments on a binary mixture of chemically identical single-chain surfactants of two different lengths at the air-water interface. However, its dynamical aspects have not been investigated so far.

C. Hybrid Models

In this model the binary mixture of A (say, oil) and B (say, water) is represented by a continuum field $\psi(\vec{r})$ in the same fashion as outlined in section 2 in the context of the continuum description of binary alloys. However, unlike the continuum model discussed in the preceding section, the amphiphiles are treated at the molecular level by describing the dynamics of the positions of the center of gravity and the orientations of the molecules. That is why this model is called “hybrid”.

In this model the surfactant molecules are modelled as “dumbbells” of length l which have two interactions

centers at the two ends, one of which is A -philic and the other is B -philic. Kawakatsu and Kawasaki⁴⁴ assumed that the “ A -philic and B -philic interactions centers of the surfactant have the same chemical species as A and B components of the binary mixture, respectively”. Suppose, the position of the center of gravity of the i -th surfactant molecule is denoted by \vec{r}_i and the unit vector from the B -philic interaction center to the A -philic interaction center of the same molecule by the symbol \hat{s}_i . For simplicity, also assume that $V_{AA}(\vec{r}) = V_{BB}(\vec{r}) = \phi(\vec{r})$ and $V_{AB}(\vec{r}) = \chi(\vec{r})$. Then, the free energy functional is given by

$$F = F_{\psi\psi} + F_{\psi s} + F_{ss} \quad (18)$$

where

$$F_{\psi\psi} = \int d^d r [(1/2)C_\psi \{\nabla\psi(\vec{r})\}^2 + (-r_o)\psi^2(\vec{r}) + u\psi^4(\vec{r})] \quad (19)$$

$$F_{\psi s} = \mu_s N_s + (ql/2) \sum \int d^d r V_-(\vec{r} - \vec{r}_i) \hat{s}_i \cdot \nabla\psi(\vec{r}) \quad (20)$$

$$F_{ss} = q^2 \sum [2V_+(r_{ij}) + (l^2/4)(s_{ij}^- s_{ij}^-) \nabla\nabla\phi(r_{ij}) + (l^2/4)(s_{ij}^+ s_{ij}^+) \nabla\nabla\chi(r_{ij})] \quad (21)$$

with

$$V_\pm(r) = \phi(r) \pm \chi(r) \quad (22)$$

$$s_{ij}^\pm = \hat{s}_i \pm \hat{s}_j \quad (23)$$

$$r_{ij} = |\vec{r}_i - \vec{r}_j| \quad (24)$$

$$\mu_s = q\rho \int d^d r V_+(\vec{r}) \quad (25)$$

where

$$\rho = \rho_A(\vec{r}) + \rho_B(\vec{r}) \quad (26)$$

is assumed to be a constant. The equations of motion are given by

$$\partial\psi(\vec{r}, t)/\partial t = L_\psi \nabla^2 [\delta F/\delta\psi] \quad (27)$$

$$d\vec{r}_i(t)/dt = -L_\rho (\partial F/\partial \vec{r}_i) \quad (28)$$

$$d\hat{s}_i(t)/dt = -L_s [(\partial F/\partial \hat{s}_i) - \{(\partial F/\partial \hat{s}_i) \cdot \hat{s}_i\} \hat{s}_i] \quad (29)$$

where L 's are phenomenological kinetic coefficients. The second term on the right hand side of the Eq. (29) arises from the constraint $|\hat{s}_i| = 1$. The Eqs. (27)-(29) were

solved numerically assuming the forms $\phi(r) = -\exp(-r)$ and $\chi(r) = \alpha \exp(-r)$. Equation (27) was solved by the cell dynamic method whereas Eqs. (28) and (29) were solved by the molecular dynamic method (see the original paper for the numerical values of the various parameters). Two kinds of initial conditions were used: (a) in case of equal volume fractions of the A and B components a random bicontinuous structure formed and coarsened with time (b) in the case where the volume fraction of the B component were three times that of the A component a dispersion of droplets was formed which coarsened with time.

In both the situations (a) and (b) mentioned above, Kawakatsu and Kawasaki⁴⁵ found a crossover in the temporal evolution of $R(t)$ from the power law $R(t) \sim t^{1/3}$ to a slower growth. Such a crossover was found to occur when the oil-water interface gets saturated by the surfactants.

Kawakatsu et al.⁴⁶ have also studied phase separation in immiscible binary mixtures in the presence of surfactant molecules of asymmetric shape using the hybrid model. They observed a spontaneous morphological change from a bicontinuous structure to a micellar structure during the phase separation process which gives rise to the formation of an amphiphilic monolayer at the oil-water interface. This is consistent with the known fact that the asymmetry of molecular shape gives rise to spontaneous curvature of amphiphilic monolayers⁴⁷⁻⁵².

D. Purely Phenomenological Models

This model is an extension of the continuum model of binary alloy phase ordering. Naturally, this is an appropriate extension of Eqs. (2)-(4) above. Suppose $\rho(\vec{r})$ is the density of the surfactant molecules at the location \vec{r} . Laradji et al.^{53,54} postulated that the effective free energy functional for the ternary system under consideration is given by

$$F[\psi(r), \rho(r)] = \int d^d r [c(\nabla\psi)^2 - r_o\psi^2 + u\psi^4 + g\rho^2\psi^2 + a\rho^2 - \mu\rho - (\Delta\mu)\psi + F_s] \quad (30)$$

Here $\rho(r)$ is the density of the surfactant molecules at the location r . c, r_o, u, g, a and μ are phenomenological coefficients. μ is the chemical potential of the amphiphilic molecules. $\Delta\mu$ is the difference of the chemical potentials of water and oil. Note that g is the strength of the coupling between the two fields ρ and ψ and Eq.(30) is an extension of equation (2). The equations of motion in this model are given by

$$\partial\psi/\partial t = \nabla^2(\delta F/\delta\psi) + \eta_\psi(\vec{r}, t) \quad (31)$$

$$\partial\rho/\partial t = \nabla^2(\delta F/\delta\rho) + \eta_\rho(\vec{r}, t) \quad (32)$$

where

$$< \eta(\vec{r}, t) \eta(\vec{r}', t') = 2k_B T \nabla^2 \delta(\vec{r} - \vec{r}') \delta(t - t') \quad (33)$$

The above equations (31)-(33) are the generalizations of the Eqs. (3) and (4). In the terminology of the Hohenberg-Halperin classification scheme²⁵ this model corresponds to the model D. The surfactant property of the amphiphiles is taken into account through

$$F_s = s \int d^d r \rho (\nabla \psi)^2 \quad (34)$$

where s is a phenomenological constant. Laradji et al.¹⁵ solved the Eqs. (30)-(33) numerically (see the original paper for the numerical values of the parameters) starting from a random initial condition, i.e., to each grid point $\psi(\vec{r})$ and $\rho(\vec{r})$ were assigned small random values around their initial values at $t = 0$. The second moment of circularly averaged structure factor, $R^{-1}(t)$, was monitored as a function of time t . The main results of their investigations are as follows: (i) The location of the peak of the structure factor moves initially to small k as time passes, thereby indicating coarsening. However, the coarsening seems to come to a halt at very late stages because the peak position was observed to become static at a fixed $k = k_e \neq 0$. Moreover, the larger is the concentration of the surfactants, the smaller is the final size of the oil-rich (or water-rich) domains. (ii) $R(t) \propto (\log t)^y$, although estimation of y was not carried out by these authors. The slow growth observed in this study is consistent with the corresponding results of the microscopic models in the preceding section.

Recently, Ahluwalia and Puri⁵⁵ have made an attempt to study the kinetics of phase ordering in ternary microemulsions using a CDS approach. The results are consistent with those obtained by the other methods discussed so far.

IV. SUMMARY AND CONCLUSION

For the description of those phenomena which are strongly dependent on steric interactions, the Larson model is believed to be more realistic than the lattice model of Kawakatsu and Kawasaki. However, if these two models belong to the same dynamic universality class, then the long-time regime, where Kawakatsu and Kawasaki have observed non-algebraic slow growth, must be lying beyond the longest runs made by Bernardes et al.⁴¹.

It is worth mentioning here that the hybrid model takes into account the surfactant property of amphiphilic molecules in a much more realistic manner than that in the purely phenomenological models. Nevertheless, the hybrid model suffers from the shortcomings that the excluded volume of the surfactants is not taken into account because of the assumption that $\rho_A(\vec{r}) + \rho_B(\vec{r}) = \text{constant}$.

The amphiphilic molecules in ternary microemulsions and micellar solutions may be regarded as impurities added to an immiscible binary mixture of oil and water. But, these are not "quenched" impurities and, therefore, the process of phase ordering is not driven by thermally activated motion of the oil-water interface. Almost all the numerical works published so far demonstrate that during the late stages of the coarsening process the oil-water interface is saturated by the surfactants leading to a reduction of the oil-water interfacial tension which gives rise to the crossover from the Lifshitz-Slyozov-like power-law growth to a slower growth of the ordered regions. This is consistent with the results obtained by incorporating the effects of the surfactants in the Lifshitz-Slyozov theory for the kinetics of phase ordering in immiscible binary mixtures⁵⁶.

Experimental study of the kinetics of ordering in ternary microemulsions and micellar solutions is difficult because this phenomenon is too fast to observe over time scales which would be sufficient to extract the growth laws. $A - B$ diblock copolymer in a A/B binary homopolymer blend behaves effectively like a surfactant because the A (B) subchain of the copolymer dissolves preferentially in the A -rich (B -rich) phase⁵⁷. Since the phase separation process in polymer systems is much slower because of entanglements of the polymer chains, the kinetics of ordering in a binary polymer blend containing an amphiphilic block copolymer can be utilized for experimental investigations. The results of such investigations can be compared with the theories of the kinetics of phase ordering in ternary microemulsions and micellar solutions.

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